

Present and Future of Polymers in Space*

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POLYMERS IN SPACE (Jet Propulsion Lab.)
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Introduction

Polymers are extensively used on spacecraft and are affected by the environment of outer space. Plastics, elastomers, and organic coatings must be tested here on earth and the results extrapolated to space environments. Therefore it is important to bear in mind that the region of space considered is not homogeneous and the composition of the gas at 200 km from earth is very different from the composition at higher altitudes. Thus the effects of space environment will depend a great deal on the particular orbit of the space vehicle. However, in most space missions three important effects must be considered, namely the effects of radiation, vacuum and temperature.

I. Radiation

Two main kinds of radiation are encountered: 1) electromagnetic radiation, or radiation from the sun, the intensity of which varies as the square of the distance from the sun; 2) radiation due to impinging atomic particles, e.g. ions and electrons. This type of radiation originates mainly from the Van Allen belt which extends from a few km to about a 1000 km above the earth.

a. Effects of Electromagnetic Radiation:

Approximately half the energy of sunlight lies in the infrared and radio frequency regions, 40% in the visible (4000-7000 Å), and 10%

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in the ultraviolet and X-ray spectral region. The latter does not pass through the earth's atmosphere but will be encountered in space.

The penetration depth of electromagnetic radiation varies with its wavelength. In the gamma-ray region at wavelength below 10^{-1} \AA this may reach 10 cm. For wavelengths between 100 and 1000 \AA penetration in solids is very small (10^{-4} to 10^{-7} cm). Near 3000 \AA the penetration into plastics may be again of the order of 10 cm. Photons of 500 to 3000 \AA cause ionization or electronic excitation, i.e. they raise electrons to higher energy states. Sunlight above 3000 \AA is not likely to damage any polymers, thus only the solar radiation that does not reach the earth's surface is of concern. The radiation between 100 - 1000 \AA which penetrates layers of 10^{-4} to 10^{-7} cm damages thin layers of all known polymers. The electronic excitation due to the effects of electromagnetic radiation results in formation of free radicals and, consequently, breakdown of polymer chains and crosslinking. Chain breakdown is accompanied by loss of mechanical strength and deterioration of electrical properties. Crosslinking reduces elastic deflection and is therefore not desirable. It eventually embrittles polymers to the point where surface flaking and fracture occur. No direct experiments have been reported on irradiation of polymers with wavelengths of the order of 100 - 1000 \AA , but experiments on irradiation at 1000 - 3000 \AA exist. Films of commercial phenyl methyl silicone, vinyl chloride and methyl methacrylate underwent appreciable crosslinking on exposure equivalent to a few days in space sunlight. At exposures corresponding to a week or two in space, polyethylene terephthalate (mylar), plasticized polyvinyl chloride and polytetrafluoroethylene were discolored and lost much of their mechanical strength and flexibility. In general, radiation in presence of air causes more damage

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than radiation in vacuum. Also, the exposure time at which a given damage is reached in vacuum may be increased three to ten times by addition of stabilizers.

b. The Van Allen Radiation Belt

In the radiation belt damage results from protons, ions and electrons which penetrate materials to a definite depth. The main effect of particle impact is ionization. The radiation doses producing appreciable change in engineering properties of various polymers are shown in Table I. The results of Table I are mainly based on effects on elongation since the tensile strength falls off with decrease of elongation.

Some correlations between polymer structure and radiation effects have been established; aromatic groups in side chains increase radiation stability over that of linear polyethylene, but aromatic groups in the main chain or ether and sulfide linkages decrease stability. Chlorine and fluorine attached to the chain reduce radiation resistance. Silicone chains are as stable as straight carbon chains.²

Reinforcement generally increases stability. Reinforced plastics are up to 10^3 times as resistant to radiation as unreinforced plastics, and carbon black improves the radiation resistance of natural rubber.³

Table I

Radiation Dose Producing Appreciable Change in Engineering
Properties of Various Polymers¹

Polymer	Ionization erg/g
Styrene, reinforced	10^{11}
Vinyl carbazol	10^{10}
Silicone resin, reinforced	10^{10}
Styrene, unreinforced	10^{10}
Ethylene terephthalate, stretched	10^{10}
Melamine, reinforced	10^9
Diphenyl silicone elastomer	10^9
Ethylene, low density	10^9
Phenolic, unreinforced	10^9
Urea formaldehyde, reinforced	10^9
Natural rubber	10^9
Vinyl pyridine	10^9
Vinyl chloride	10^9
Vinylidene chloride	10^9
Silicone resin, unreinforced	10^9
Butadiene-styrene (SBR)	10^9
Ethylene, high density	10^8
Propylene	10^8
Vinylidene fluoride-hexafluoropropene	10^8
Chlorotrifluoroethylene-vinylidene fluoride	10^8
Ester, unreinforced	10^8
Butadiene-acrylonitrile (nitrile rubber)	10^8
Butadiene	10^8
Neoprene (chloroprene)	10^8
Chlorosulfonated ethylene	10^8
Acrylic	10^8
Silicone elastomers (most)	10^8
Nylon	10^8
Polyformaldehyde	10^7
Isobutylene-isoprene (butyl rubber)	10^7
Silicone elastomer, fluorinated	10^7
Tetrafluoroethylene	10^6

II. Vacuum Effects

At the altitude of 200 kms the gas pressure is of the order of 10^{-6} mm Hg and decreases at higher altitude (10^{-13} at 6500 km). Any low molecular weight compounds such as plasticizers or fragments produced as a result of radiation damage would volatilize. The temperature at which a 10% weight loss occurs, for a variety of polymers, is tabulated below (Table II).

The volatilization of materials endangers the function of the spacecraft since the volatiles may redeposit on cool surfaces, e.g. relay contacts and prevent them from closing properly.

The simplest quantitative value which can be obtained for the behavior of a polymer in the thermal-vacuum environment is the loss of weight. This value does not reveal the nature of the components but nevertheless is useful for selecting polymers suitable for spacecraft, since in the majority of instances it may be safely assumed that mechanical or other useful properties of the polymer are degraded when a substantial loss of weight has been incurred. It is customary to assume that polymeric substances which lose less than 1% of their weight in a thermal-vacuum environment may be ordinary gases (e.g. adsorbed air or carbon dioxide), liquids of high vapor-pressure (e.g. lubricating oils, plasticizers). In order to select polymeric materials for Mariner IV (successful Mars probe) a volatile-condensable material (VCM) test was applied. The VCM test is a measure of the volatile materials given off by a polymer that will condense on a cooler surface. A VCM value of less than 0.5×10^{-4} gm of condensables per square inch of sample material area was considered acceptable. Over one hundred different polymers were

Table II

Decomposition of Polymers in High Vacuum

Polymer	Temperature for 10% weight loss per year in vacuum		Literature references
	°C	°F	
Nylon	30 - 210	80 - 410	4
Cellulose nitrate	40	100	5
Methyl acrylate	40 - 150	100 - 300	6
Vinyl chloride	90	190	7
Neoprene (chloroprene)	90	200	5
Methyl methacrylate	100 - 200	220 - 390	6
Acrylonitrile	120	240	8
Isobutylene-isoprene (butyl rubber)	120	250	9
Styrene-butadiene	130	270	5
Styrene	130 - 220	270 - 420	6
Butadiene-acrylonitrile (nitrile rubber)	150 - 230	300 - 450	9
Vinyl acetate	160	320	10
Cellulose	180	350	6
Methyl styrene	180 - 220	350 - 420	6
Cellulose acetate	190	370	11
Propylene	190 - 240	370 - 470	6
Isoprene	190	380	12
Melamine	190	380	13
Silicone elastomer	200	400	14
Ethylene terephthalate (mylar, dacron)	200	400	15
Isobutylene	200	400	6
Vinyl toluene	200	400	6
Butadiene-styrene (GR-S = SBR)	240	460	6
Vinyl fluoride	240	460	16
Ethylene, low density	240 - 280	460 - 540	6
Butadiene	250	490	12
Chlorotrifluoroethylene	250	490	6
Vinylidene fluoride	270	510	16
Ethylene, high density	290	560	6
Tetrafluoroethylene	380	710	16

used, after screening, in the Mariner IV spacecraft. These included teflon for wire insulation, and MoS_2 -impregnated nylon in the TV camera system, asbestos-filled epoxy adhesives and room temperature vulcanizing (RTV) silicone adhesive for the solar panels, polyvinylfluoride for cabling, multilayered aluminized mylar for thermal shields, etc.¹⁷ The successful mission of Mariner IV shows that the above polymers are suitable for relatively long space flights.

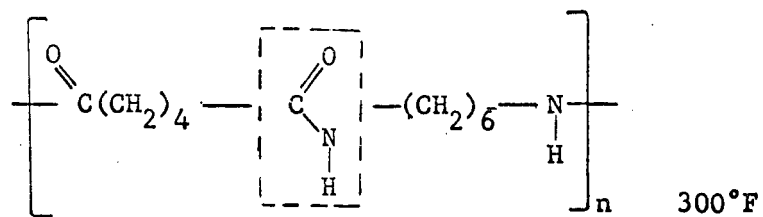
III. Temperature

The exploration of outer space requires materials that would withstand high temperatures, as well as cryogenic materials, i.e. those used for equipment and structures subjected to extremely low temperatures.

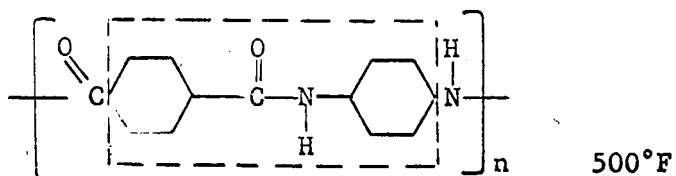
a. High Temperature Polymers

The requirements of space technology led to exciting new discoveries in the area of heat resistant polymers. Significantly higher thermal stability is obtainable from polymeric systems comprised of heterocyclic recurring units.¹⁸ The following sketches indicate the types of polymers already available commercially, and the upper temperature limits of their usability.¹⁹

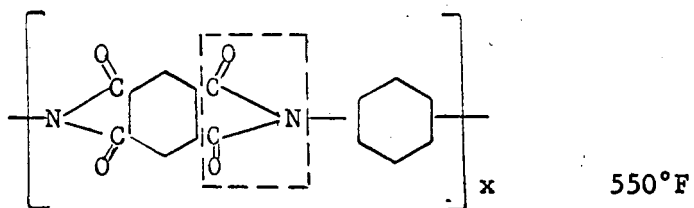
An Aliphatic Polyamide (Nylon)



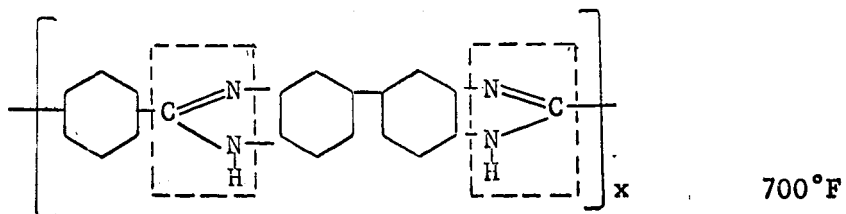
An Aromatic Polyamide (Nomex)



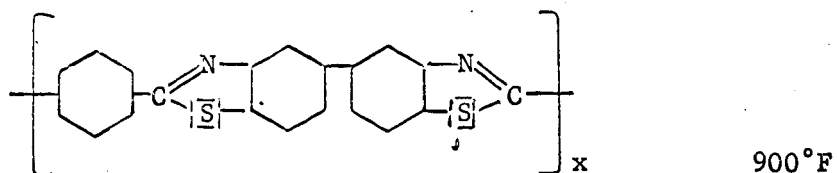
An Aromatic Polyimide (SKYGARD)



A Polybenzimidazole (IMIDITE)



Polybenzothiazoles



The thermal stability of the above polymers is due to their continuous chain stiffness and to the /conjugation of the bonds within the molecule.

b. Low Temperature Polymers

Generally, plastic materials have shown relatively good low temperature resistance. They are attractive for cryogenic applications because of their low thermal conductivity as well as specific heat and good mechanical properties. However, their high coefficient of thermal expansion constitutes a definite disadvantage. This may be overcome by the addition of finely divided metals or metallic oxides.²⁰

Polytrifluoromonoethylen (Kelf) has been used effectively at cryogenic temperature for many years for engineering applications. Although less ductile than at room temperature, the low crystallinity material still has approximately 5% elongation at -320°F .

Closed-cell rigid plastic foams have been used in cryogenic insulation systems. The foams of most interest for such applications are polystyrene, epoxy, polyurethane and rubber.²¹

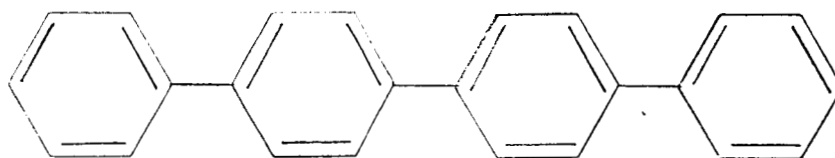
Most commonly used cryogenic seals are made of fluorinated polymers but mylar and nylon have been found usable as gaskets from -323 to 350°F .

Elastomers, with the exception of certain silicones and fluorosilicones which can operate as low as -120°F , generally have unsatisfactory mechanical properties due to extreme brittleness at temperatures below -70°F . Plastics, of low glass transition temperatures and high crystallinity are able to withstand much lower temperatures without sacrificing their original resiliency, hardness and impact strength.

IV. Future Trends

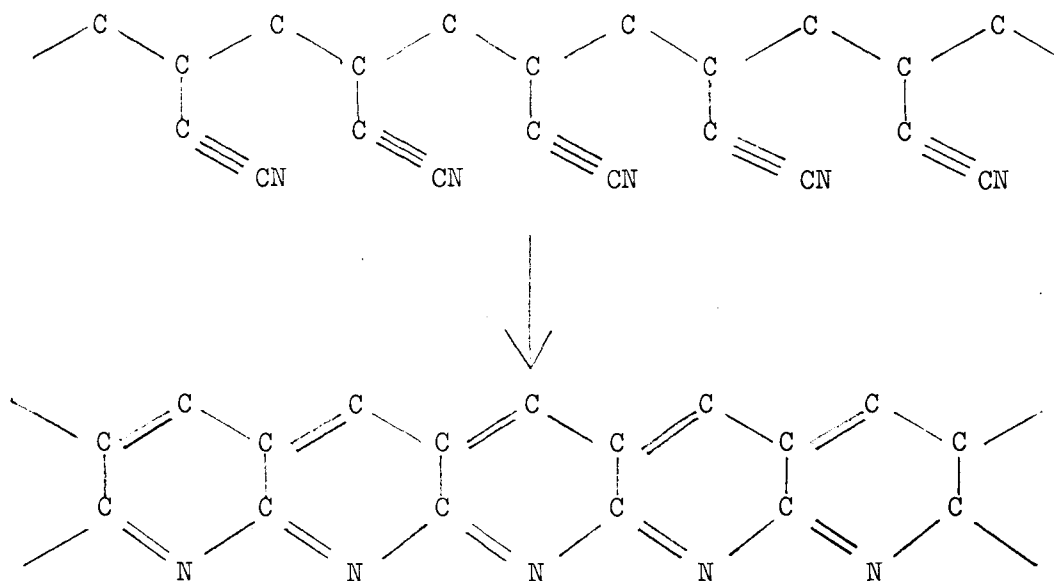
a. Thermally Stable Polymers

A great deal of research effort is being expended toward the synthesis of new thermally resistant polymers. The polybenzimidazoles can withstand temperatures of up to 500°C for long periods of time without softening and deterioration. One reason for their high thermal stability is the rigidity of the chains due to large aromatic recurring units. Other rigid molecules which are now being studied for possible applications in the field of high temperature resistant materials are based on other aromatic chains such as polyphenylene,²²



Polyphenylene

which cannot fold even at rather high temperatures because rotation about the carbon-carbon single bond between the para-combined phenylene rings can only lead to different angles between the planes of consecutive rings but not to a kink or bend in the main chain. The presently available polyphenylenes are characterized by low molecular weight but there is little doubt that future research will lead to the synthesis of high molecular weight polyphenyls, and consequently greatly improved mechanical properties. Another interesting way to arrive at chains made up of condensed rings is the synthesis of so-called ladder polymers. The first example of such a structure was prepared by exposing polyacrylonitrile to elevated temperatures which caused the formation of rows of six rings by an electron pair displacement.

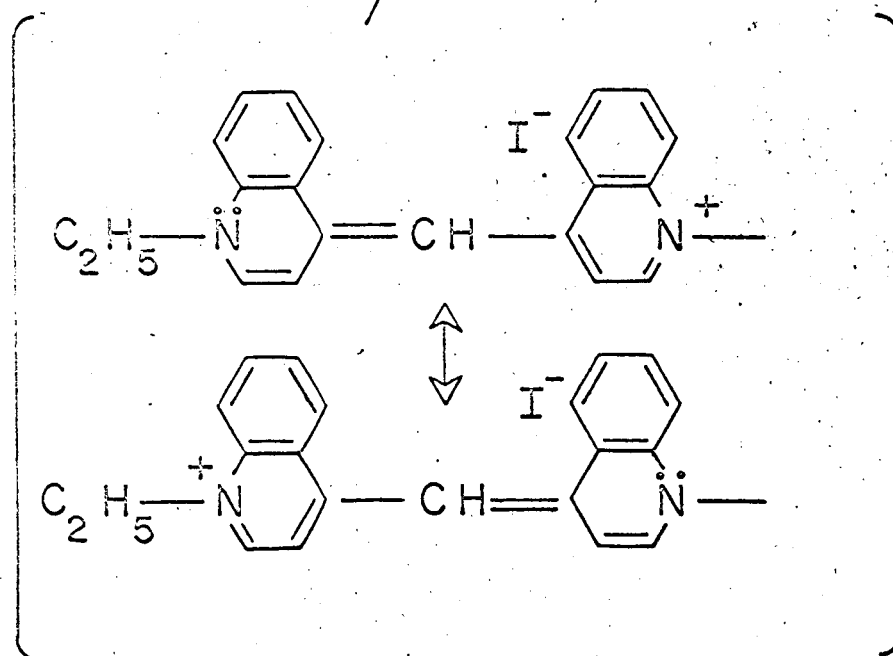
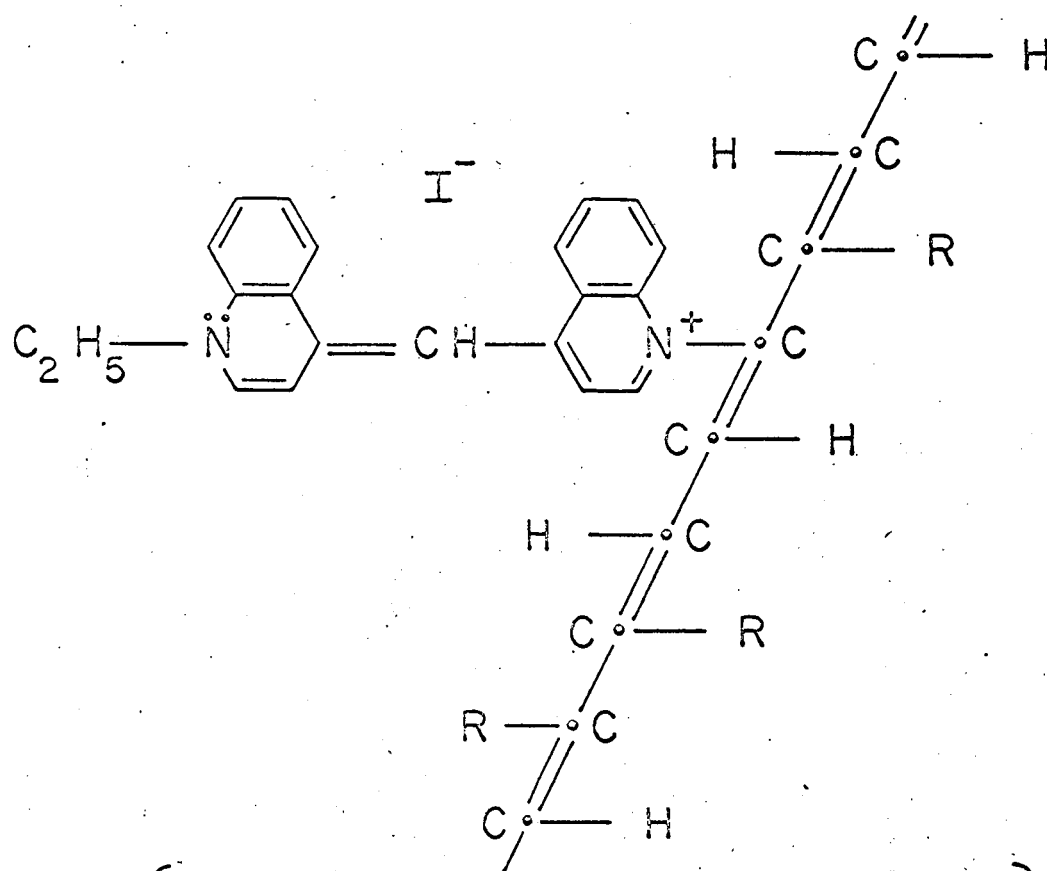


A black, completely infusible and insoluble material is obtained which corresponds in its structure to a linear graphite in which one carbon atom of every ring has been replaced by nitrogen. The rigidity and stiffness of chains as well as the fact that two bonds need to be broken in a ladder polymer instead of one as in conventional polymers, indicate that this type of material is very promising for space as well as for many industrial applications. One may therefore expect a great deal of activity in this area in academic as well as in commercial institutions.

b. Solid Propellants

Polymers are extensively used as binders for inorganic oxidizers in solid propellants. At the early stages of solid propellant chemistry, thermoplastic or thermosetting polymers were already used as binder fuel. They consisted of phenolic resins, polystyrene copolymers, cellulose polymers, styrene, butadiene-rubber, etc.²³

A desirable solid propellant binder should consist of a viscous fluid allowing easy mixing with the oxidizer (e.g. ammonium perchlorate). It is necessary after the mixing operation to transform the viscous slurry into a solid rubbery material. These requirements were met by polyurethanes and from 1954 until recently polyurethane was the most important solid propellant binder for rocket application. About six years ago a solid propellant using polybutadiene acrylic acid copolymer was developed. This polymer was the first of polybutadiene rubbers used in the solid rocketry area but later a number of other rubbery polymers were found. One of the most interesting in this category consists of polybutadiene terminated at both ends by carboxyl groups and synthesized by the "living polymer" technique. Solid propellant for future use in space missions must offer higher performance and at the same time withstand the special environmental conditions imposed by such missions. Improved performance will be obtained by the use of either better oxidizers or specially developed polymeric binders or both. New polymeric binders are required to make them compatible with high energy ingredients and permit simultaneously a high solid loading. Future developments of improved solid propellants will depend on the fact that planetary spacecraft intended to land on Mars, Venus, Mercury, Jupiter, etc. must undergo a sterilization treatment to prevent contamination of planets with Earth organisms. If the sterilization requirements do not change, then the new propellants will have to withstand three 36-hour cycles of heating at 145°C (293°F) and retain high reliability. In order to operate at low temperature to which the solid propellant may be exposed in space, the binder should exhibit a low glass transition temperature. Apart



from the above conditions it will be necessary to have a binder undergoing a negligible vaporization loss in a high vacuum.

c. Superconducting Polymers

In 1950 a suggestion was made by F. London²⁴ that some of the more complicated organic molecules might be able to exhibit, not semiconductivity but superconductivity. This idea was taken up in 1964 by W. A. Little²⁵ who postulated on the basis of the B.C.S. theory that a polymer of the structure shown below may exhibit superconductivity at room temperature. Synthesis of such a material would lead not only to tremendous developments in the polymer industry but also to a revolution in our own way of life.

A superconducting polymer could solve a number of difficult space problems, in particular the prevention of communication blackout of a space vehicle during reentry. Although the synthesis of a superconducting polymer having a structure shown above is by no means an easy task, it is likely to be achieved in the future, and if indeed such polymers superconduct at room temperature, practically an unlimited number of applications on our planet as well as in space can be envisioned.

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